Maryland Department of Natural Resources
Non-tidal Network Program
Nutrient and Sediment Trend Monitoring

QUALITY ASSURANCE PROJECT PLAN
July 1, 2005 - June 30, 2006

SECTION 117(d)

MARYLAND DEPARTMENT OF NATURAL RESOURCES
RESOURCE ASSESSMENT SERVICE
MONITORING AND NON-TIDAL ASSESSMENT DIVISION

Maryland Department of Natural Resources
Non-tidal Network
Nutrient and Sediment Load Trend Monitoring
Quality Assurance Project Plan
July1, 2005 – June 30, 2006
Section 117(d)

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Preface

Maryland's Non-tidal Water Quality Monitoring Network began in July 2004 with funding from EPA Section 117(d). The network, presently, is composed of 10 sites where nutrient and sediment concentrations are sampled on a fixed monthly basis and 8 times during high flow events. Monthly sampling only is performed at an additional 4 locations. All sampling sites are located near a USGS stream gage, have a nearby bridge from which high flow samples may be obtained, are located at the outlet of major basins and represent watersheds with relatively high loads of nutrients and sediments.

Maryland's network was created as part of a coordinated effort, conducted by the Chesapeake Bay Program's Non-tidal Workgroup, to include all of the Chesapeake Bay watershed states in a network of stations with comparable collection and analyses protocols. Data from the Non-tidal Network will be used to estimate nutrient and sediment loads and trends in concentration for watershed management assessment purposes and for input to the CBP Watershed Model.

It is anticipated that the Non-tidal Network may be expanded spatially and upgraded (by sampling nutrients and sediment concentrations during high flow events at all sites) as more funding becomes available.

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ACRONYMS AND ABBREVIATIONS

AMQAW - Analytical Methods and Quality Assurance Workgroup (a workgroup of the Chesapeake Bay Program's Monitoring Subcommittee)
C - carbon
CBP - EPA's Chesapeake Bay Program
CBPO - EPA's Chesapeake Bay Program Office
CBL - University of Maryland's Chesapeake Biological Laboratory
cm - centimeter
CSSP - Coordinated Split Sample Program
DHMH - Maryland Department of Health and Mental Hygiene
DNR - Maryland Department of Natural Resources
DO - dissolved oxygen
DOC - dissolved organic carbon
EPA - U.S. Environmental Protection Agency
g - gram
H_2O - dihydrogen oxide (water)
L - liter
m - meter
MDE - Maryland Department of the Environment
min. - minute
mg - milligram
ml - milliliter
mm - millimeter
N - nitrogen
NIST - National Institute of Science and Technology
NO_2 - nitrite
$NO_{2,3}$ - nitrate + nitrite
NO_3 - nitrate
P - phosphorus
PC - particulate carbon
PN - particulate nitrogen
PO_4 - phosphate
PP - particulate phosphorus
QAO -Quality Assurance Officer (unless otherwise noted, this refers to the DNR QAO)
QAPP - Quality Assurance Project Plan
RP - replicate
TDN - total dissolved nitrogen
TDP - total dissolved phosphorus
TSS - total suspended solids
USGS - U.S. Geological Survey
^oC - degrees Celsius

Distribution List

Mary Ellen Ley, USGS/Chesapeake Bay Program
Steve Preston, USGS/Chesapeake Bay Program
Bruce Michael, MDNR
Sally Bowen MDNR
Paul Miller, MDNR
Tony Allred, MDNR
Bill Romano, MDNR
Scott Phillips, USGS

PROJECT MANAGEMENT

A4 Project Organization and Responsibility

This section lists the individuals responsible for the major aspects of the CBP Non-tidal Network Program. The flow of project tasks is indicated in Figure 1.

Director and Principal Investigator: Bruce Michael, Tidewater Ecosystem Assessment, DNR. 410-260-8627, bmichael@dnr.state.md.us

Responsibilities: The director and principal investigator is responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other DNR managers and coordination with cooperating agencies and institutions. This individual is also responsible for the technical design, conduct and data analysis of the program.

Quality Assurance Officer: Bruce Michael, Tidewater Ecosystem Assessment, DNR. 410-260-8627, bmichael@dnr.state.md.us

Responsibilities: The quality assurance officer is responsible for documenting and assuring the conduct of field, laboratory and data management procedures that comprise this study.

Field Sampling Operations: Sally Bowen, Project Chief, Monitoring Field Office. Monitoring and Non-tidal Assessment, DNR. 410-990-2528, sbowen@dnr.state.md.us

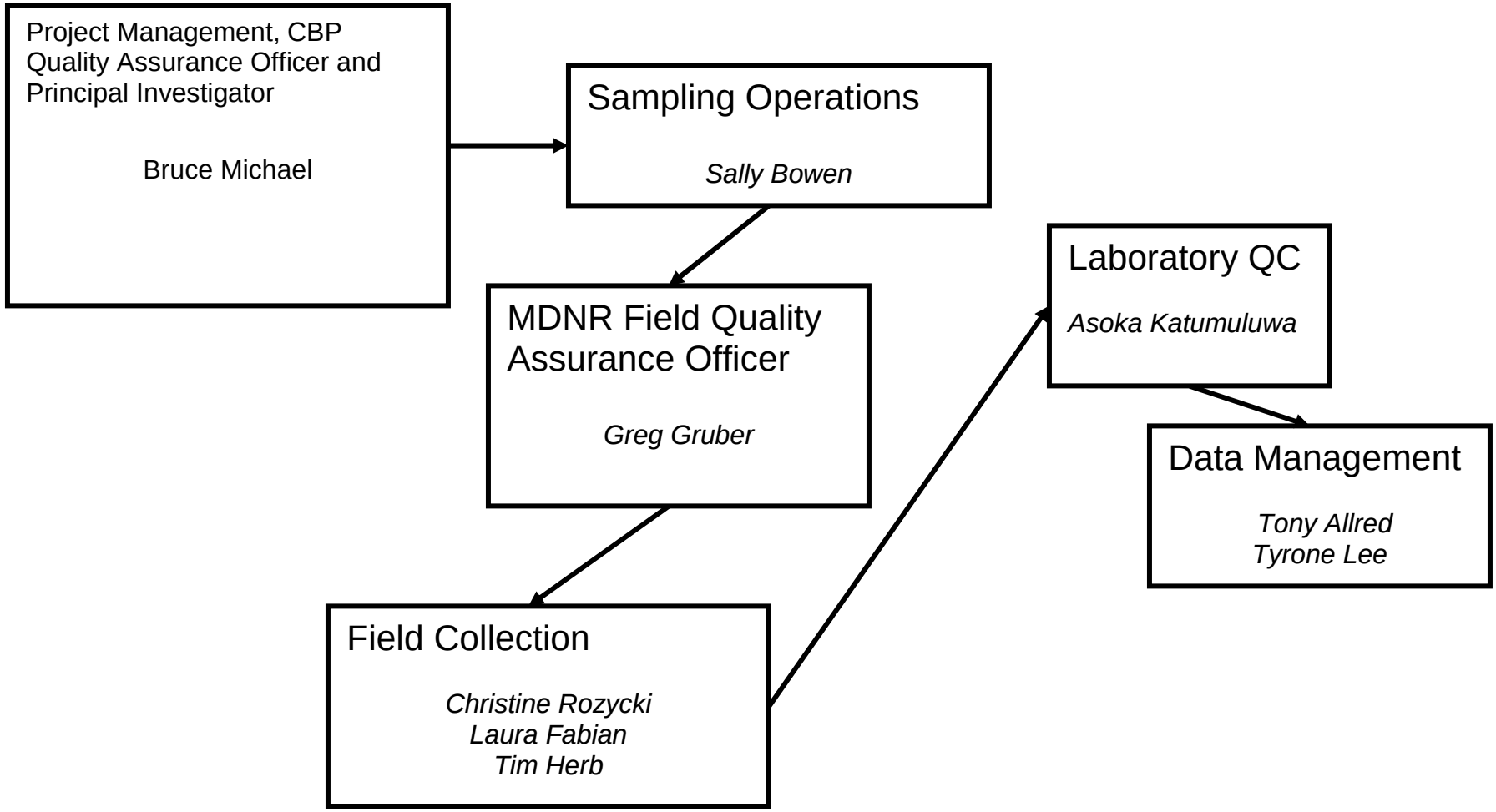
Responsibilities: This individual is responsible for administration of the field sampling activities including sample collection, sample storage and sample delivery to laboratories.

Laboratory Analyses/Water Column Chemistry: Asoka Katumuluwa, Public Health Laboratory Principal Scientist Developmental, DHMH. 410-767-5034, katumuluwaa@dhmh.state.md.us

Responsibilities: This person oversees the laboratory that does all of the nutrient analysis and water chemistry for the project.

Data Management; Tony Allred/Tyrone Lee, Maryland Department of Natural Resources. 410-260-8642/410-260-8643, tallred@dnr.state.md.us tlee@dnr.state.md.us

Figure 1. Organization Chart for the Maryland 117(d) Non-tidal Network Project



Responsibilities: These individuals are responsible for overseeing the management of field and laboratory data collected under this program; managing historical field and laboratory data collected under this program; and maintaining existing data management software.

Sediment Analysis: Libby Shreve. USGS Kentucky Water Science Center. 502-493-1900, eashreve@usgs.gov .

Responsibilities: Determine suspended sediment concentration and sand/fine fractions on high flow event samples.

A5 Project Background

The Chesapeake Bay Program, under the Chesapeake 2000 agreement, is committed to reduce nutrient and sediment inputs into Chesapeake Bay. Nutrient and sediment allocations have been developed for tributary basins within the Bay watershed. This project is part of the co-operative effort of the Chesapeake Bay Program Non-tidal Workgroup to provide comparable data to assess progress in meeting nutrient and sediment reduction goals to meet water quality criteria in the Chesapeake Bay. The main objective of this monitoring program is to improve measurement of nutrients and sediment concentrations in the Chesapeake Bay watershed. The project requires all participants to collect samples by a method that generates horizontally and vertically integrated, flow weighted composite samples. This standard USGS collection method should provide data that better represents the concentration of nutrients and sediments. Since this project will specifically collect samples from eight rain events per year, our estimates of sediment loads contributed by or ten primary watersheds should be greatly improved.

Historically, Maryland's collection method at non-tidal sites was a single point grab sample. We will continue to collect a single point grab sample under our CORE/TREND Network at historically collected locations. We will collect an integrated sample every month under the Non-tidal Network using the USGS isokinetic sampling device if maximum velocity is 1.5 ft/sec of higher. A review of USGS discharge records indicates that for the majority of our stations, base and maximum flow is normally under 1.5 fps. Under low velocity conditions, a horizontal and vertically and depth integrated composite sample will be generated. We anticipate that we will only collect isokinetic, flow weighted samples during significant storm events. The stations where maximum velocity sometimes exceeds 1.5 fps during base flow are ANT0047, WIL0013, GEO0009 and, perhaps, DER0015.

Monthly measurements of in-situ parameters have also indicated that all sites except WIL0013 are well mixed. Since most of our sites are less than 110 feet wide, most are 3 feet or less in depth and most have a velocity under 1.5 fps, our historical data set

may be a reasonable representation of dry weather conditions. When using the historical data, discarding dates with an elevated discharge reading would provide data that is more representative of baseflow conditions.

Sites in the Maryland CBP Non-tidal network are listed in Table 1 and located on Figure 2. Monthly sampling is performed at all sites. Sites classified as "primary" have, in addition to monthly sampling, approximately 8 samples taken during high flow events (defined in this project as a 10 fold increase in flow). These additional "storm" samples provide site-specific information on the relationship between discharge and concentration necessary for load estimations. Site selection for both primary and supplemental (monthly sampling only) was based upon 1) the presence of an operating stream gauge, 2) sites located at the outlet of a tributary strategy basin, 3) sites representing high load watersheds, 4) watershed area and 5) the presence of a bridge for sampling during high flow events.

A6 Project Description

Sample collection and analysis began in July 2005. The network contains 10 primary sites and 4 supplemental sites (Table 1). Monthly sampling is conducted at both primary and supplemental sites. Eight samples during high flow conditions will be taken at primary sites each year.

Depth integrated samples will be taken at equal width intervals and composited at both primary and supplemental sites any time the site is sampled for the non-tidal project.

Parameters and analytical methods are listed in Table 2. An additional sample will be taken from a churn splitter for sediment concentration and sand/fine analysis any time high flow conditions are sampled.

The data will be stored on the Maryland DNR server on Tawesdata 2 directory and submitted annually to the CBP for inclusion in the non-tidal water-quality database of the Chesapeake Information Management System (CIMS).

A7 Quality Objectives and Criteria

Representativeness: Monthly fixed interval sampling is adequate for capturing long-term annual trends in concentration. Eight additional samples taken during high flow events are intended to determine the relationship between stream discharge and the parameters of interest so that annual loads may be calculated for primary sites.

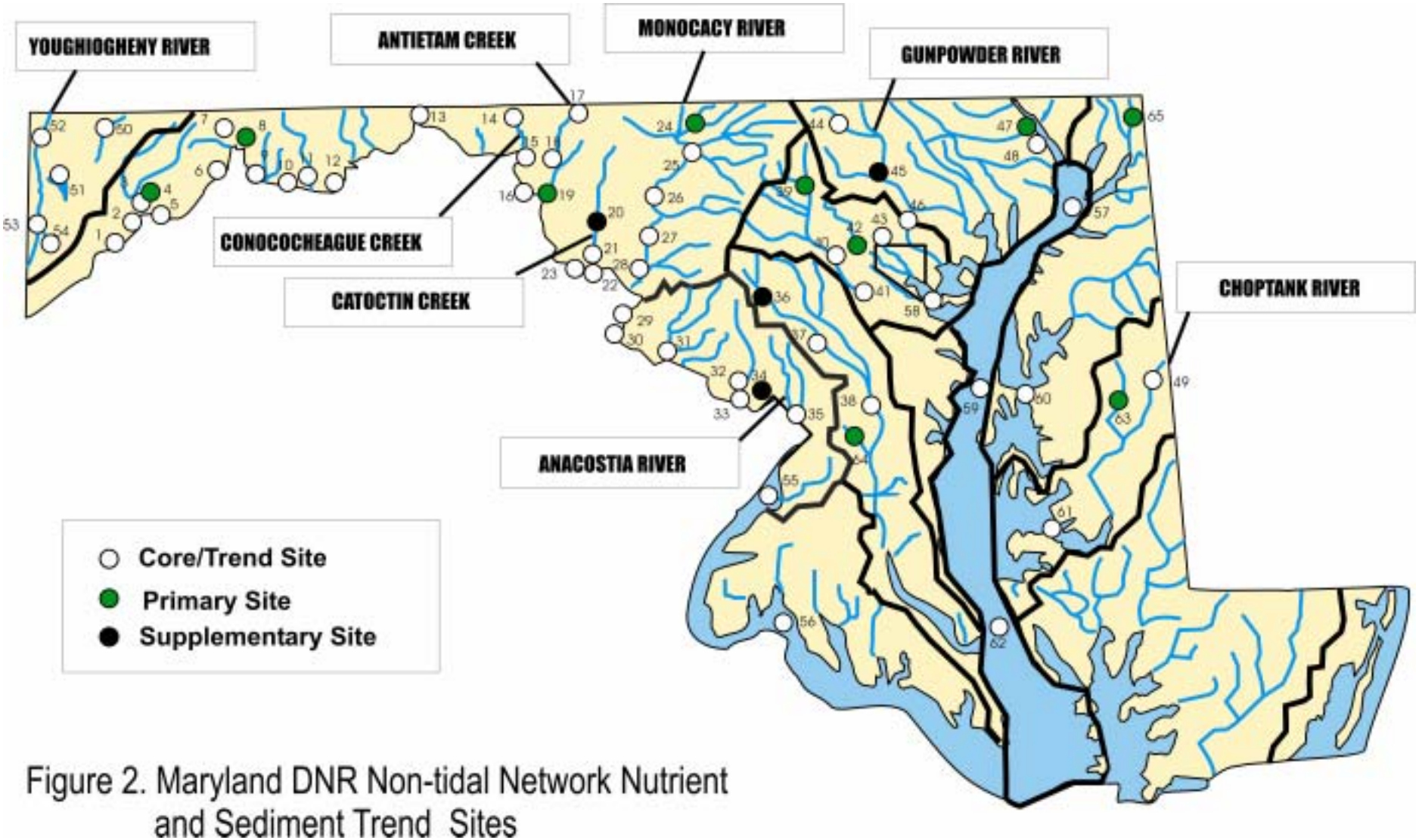


Figure 2. Maryland DNR Non-tidal Network Nutrient and Sediment Trend Sites

TABLE 1. Maryland CBP Non-tidal Network Program

Map #	MDNR Station ID	Stream Name	Lat (NAD83)	Long (NAD83)	Description of Sampling Location	USGS Gauge #	Network Station Type
4	GEO0009	Georges Creek	39 29.6183083	079 02.6819417	Victory Street in Westernport, MD	01599000	Primary
8	WIL0013	Wills Creek	39 39.7110433	078 46.8174567	Locust Grove Road crossing Wills Creek in Cumberland, MD	01601500	Primary
19	ANT0047	Antietam Creek	39 27.240000	077 43.965	Burnside Bridge Road near Sharpsburg	01619500	Primary
20	CAC0148	Catoctin Creek	39 19.9069327	077 34.8107379	At bridge on MD 17	01637500	Supplemental
24	MON0546	Monocacy River	39 41.7870000	077 14.368000	Bullfrog Road crossing the Monocacy	01639000	Primary
34	RCM0111	Rock Creek	38 59.5812919	077 03.7817405	At bridge on MD 410	01648000	Supplemental
36	PXT0972	Patuxent River	39 14.3584867	077 03.3713467	At bridge on MD 97 near Unity	01591000	Supplemental
39	NPA0165	North Branch Patapsco River	39 28.9671333	076 52.9250800	Upstream of bridge at MD 91	01586000	Primary
42	GWN0115	Gwynns Falls	39 20.5671783	076 43.5833000	At bridge on Essex Road in Villa Nova	01589300	Primary
45	GUN0258	Gunpowder Falls	39 33.0386351	076 38.1520258	Confluence of Upper and Lower Glencoe Road at girder bridge	01582500	Supplemental
47	DER0015	Deer Creek	39 37.4085651	076 09.8863317	Bridge at Stafford Bridge Road	01580000	Primary
63	TUK0181	Tuckahoe Creek	38 58.0280000	075 56.5870000	Tuckahoe Creek at Crouse Mill Rd.	01491500	Primary
64	TF1.2	Western Branch	38 48.8580017	076 45.05207	At bridge on Water St. in Upper Marlboro	01594526	Primary
65	BEL0053	Big Elk Creek	39 37.2870000	075 49.7160000	Big Elk Creek at Rt. 279	01495000	Primary

TABLE 2. Parameters and Analytical Methods for the Chesapeake Bay Nontidal Water-Quality Network

Parameters	Holding Time and Condition	Methods	Method Detection Limit
Total Nitrogen, mg/L as N	Calculated	PN + TDN	N/A
Ammonium, mg/L as N (dissolved, unless noted)	Freeze 28 days	350.1*	0.004 mg/L
Nitrite mg/L as N	Freeze 28 days	353.2*	0.0004 mg/L
Nitrate + Nitrite, mg/L as N (dissolved, unless noted)	Freeze 28 days	353.2*	0.003 mg/L
Total Phosphorus, mg/L as P	Calculated	PP+TDP	0.01 mg/L
Orthophosphate, mg/L as P (dissolved, unless noted)	Freeze	365.1*	0.002 mg/L
Total Suspended Solids mg/L	4 ^{o}C 48 hours	SM 2540 D	0.9mg/L
Suspended Sediment (storms)	Dark Room 120 days	ASTM D3977C	0.5 mg/L
Sand/Fine Particles (storms)	Dark Room 120 days	DE 35997D	0.5 mg/L
Dissolved Oxygen (field) mg/L	N/A	In-situ	0.2 mg/L
Temperature (field) ^{o}C	N/A	In-situ	0.1 ^{o}C
Specific Conductance (field) umhos/cm	N/A	In-situ	1 umhos/cm
PH (field)	N/A	In-situ	0.1 units
Dissolved Organic Carbon mg/L as C	Freeze 28 days	EPA 415.1	0.14 mg/L
Total Dissolved Phosphorus mg/L as P	Freeze 28 days	alk. persulfate	0.006 mg/L
Total Dissolved Nitrogen mg/L as N	Freeze 28 days	alk. persulfate	0.006 mg/L
Particulate Carbon (PC) mg/L as C	Freeze 28 days	Combustion IR EPA 440.1	0.006 mg/L
Particulate Nitrogen mg/L as N	Freeze 28 days	Combustion IR EPA 440.1	0.003 mg/L
Particulate Phosphorus mg/L as P	Freeze 28 days	Digestion and flow injection	0.003 mg/L

* Dissolved parameters are prepared by filtration through a 0.7 micron glass fiber filter.

Depth integrated samples using an isokinetic sampler or a weighted bottle sample will be used at equal width intervals, the number of which are determined from Table 2. The type of sampler used is dependent upon flow velocity with the isokinetic sampler being used if the centroid flow velocity $\geq$ 1.5 ft/sec. Depth integrated samples are composited (i.e. combined for each width interval in a 4-liter churn splitter). Sample bottles for nutrient and sediment analysis are filled from the churn splitter.

Table 3. Minimum Number of Vertical at Primary Stations
(Routine and storm event samples)

Width of Waterway (ft)	Minimum # of Verticals
0-25	1
25-100	3
100-250	5
250-500	7
>500	9

Comparability: Comparability among data sets is assured through the use of consistent field methods and protocols, participation in the Analytical Methods and Quality Assurance Workgroup (AMQAW) and the use of field splits and blind audit samples.

Comparability of monitoring data is achieved as a result of quality assurance procedures at each phase of the data gathering and processing. It includes representative sampling and sample handling procedures, uniform laboratory methods and validation of laboratory data and procedures for reduction, validation and reporting of environmental data.

Completeness: To ensure that data are of the quality required to support Chesapeake Bay Program management decisions, Maryland's Chesapeake Bay Water Quality Monitoring Program strives to provide monitoring data of known and consistent quality to the CBPO by generally following the guidelines outlined in Section E of the *Recommended Guidelines for Sampling and Analysis in the Chesapeake Bay Monitoring Program, August 1996* (EPA 1996). These guidelines recommend precision goals of field and lab measurements of <20 percent of the coefficient of variation; accuracy goals within 80 to 120 percent, and the completeness goals of 100 percent.

Accuracy: The accuracy (closeness to the true value) of the collected data is controlled and assured by the proper use, calibration, and maintenance of both field and laboratory equipment for the measurement of physical and chemical parameters. All instruments are identified by a unique number, used as an index for documentation of calibration, repair, and preventive maintenance. Where possible, standards used for calibration purposes are validated against a primary standard such as those available from the National Institute of Science and Technology (NIST).

Daily quality control checks (including the running of blanks and standards) are used to control and assure laboratory accuracy.

Accuracy of laboratory results is also assessed through DNR's participation in the Chesapeake Bay Coordinated Split Sample Program (CSSP), a split sampling program in which five laboratories involved in Chesapeake Bay monitoring analyze quarterly, coordinated split samples. CSSP was established in June 1989 to establish a measure of comparability between sampling and analytical operations for water quality monitoring throughout the Chesapeake Bay and its tributaries. DNR follows the protocols in the *Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines* (EPA 1991) and its revisions. Split samples are collected quarterly. Results are analyzed by appropriate statistical methods to determine if results differ significantly among labs. When a difference occurs, discussion begins regarding techniques and potential methods changes to resolve discrepancies and identify potential problems.

Additionally, DHMH will participate two times per year in the United States Geological Survey (USGS) reference sample program and will permit USGS to release the results to the Chesapeake Bay Program Quality Assurance Officer. Laboratory accuracy is 90-110% recovery.

Precision: Precision (repeatability) of the chemical analytical methods is determined and documented from duplicate analyses. Precision of the entire measurement system for laboratory-analyzed parameters, including field processing, storage, and chemical analysis, can be assessed from duplicate field samples. Duplicate field samples are routinely collected approximately every 10 to 20 samples. The protocols for duplicate analyses in the laboratory are described in the Standard Operating Procedures for DHMH. Laboratory precision is +/- 10% RSD.

A8 Special Training/Certification

Maryland DNR field personnel participated in a two-day USGS/CBP sponsored workshop on techniques required for obtaining a representative sample of nutrient and suspended sediment concentration in Harpers Ferry, WV in September 2004.

A9 Documents and Records

Critical project personnel receive copies of the QAPP (c.f. distribution list). The QAPP will be updated annually by June 30. Project reporting to management will be accomplished by semi-annual progress reports of activities that will include tabular and electronic summaries of provisional instantaneous water quality for the reporting period.

DATA GENERATION AND ACQUISITION

B1 Program Design

Sampling locations are described in Table 1 and shown on Figure 1. In order for a site to be considered for the NTN project, it needed to: 1) have an operating stream gage, 2) represent tributary strategy basins, 3) represent watersheds with high nutrient and sediment loads, 4) be among Maryland's larger watersheds and 5) have a safe bridge from which storm samples could be taken. Stations from DNR's historical network were reviewed to see if they met these criteria and stations in under sampled regions of the state were also considered. Sampling began at five initial primary sites (MON0548, ANT0047, GEO0009, BEL0053 and TUK0181) in January 2005. Five additional primary sites (WIL0013, NPA0165, GWN0115, DER0015 and TF1.2) were chosen when additional funding became available in July 2005. The four supplemental sites all have the same attributes as primary sites and may be upgraded for storm event sampling as funding becomes available.

B2 Sampling Methods

Base flow samples: EWI, depth integrated samples are taken monthly at primary and supplemental sites. Vertical sampling is done with a DH-81 if the stream is wadable or a DH-59 (or DH-95) where samples are accessible only from a bridge. Samples are composited in a 4-liter churn splitter from which subsamples are drawn. A single whole water sample bottle is drawn and sent to DHMH for TSS analysis. A second whole water sample bottle is drawn and field processed for dissolved nutrients and particulate analysis.

Storm samples: Sampling during high flow events (i.e. a 10 fold increase in flow) is accomplished from a bridge by use of a DH-59 or DH-95 at primary sites only. All vertically integrated samples are collected in the churn splitter and, in addition to the TSS, dissolved nutrients and particulate filters for analysis at DHMH, a whole water sample is drawn to send to the USGS Sediment Laboratory in Kentucky for suspended sediment analysis.

Field Measurements: Dissolved oxygen, pH, specific conductance and temperature are measured monthly and during high flow events by using a Hydrolab. Measurements are taken at the center of each EWI and the median value is recorded for the sample. Average stream flow during the sampling period, as reported by USGS, is also recorded. See the attached Non-tidal Network Program Standard Operating Procedures for more detailed information.

B3 Sample Handling and Custody

Water quality samples are collected, field processed to generate filtrate for dissolved nutrients, filtered for particulate analysis and a single, whole water sample for TSS is

drawn directly from the churn splitter. Samples are placed on ice and transported in coolers by Department of Natural Resources (DNR) Monitoring Program field personnel to Annapolis. Samples are either frozen for later delivery or taken directly to the State laboratories by the field personnel or left with a courier for delivery to the State laboratory. Data sheets accompany these samples to the laboratory (Figure 3). Data produced from laboratory analysis and field measurements then follow a controlled pathway to computer files under the direction of a data processing manager (Figure 4).

B4 Analytical Methods

Analytical methods for baseflow and highflow event samples are described in Table 2. All Hydrolab instruments are calibrated both prior to and after their use for measuring temperature, pH, dissolved oxygen and conductivity. All calibration checks are recorded in field logbooks. Laboratory personnel follow EPA guidelines on quality control and quality assurance. Minimum detection limits for field measurements are described in Table 4.

Table 4. Minimum Detection Limits for Field Measurements

PARAMETER	MINIMUM DETECTION LIMIT
Water Temperature	0.1 ^{o}C
Depth	0.5 m
Dissolved Oxygen	0.2 mg/L
Specific Conductance	1 umhos/cm
pH	0.1 pH units

B5 Quality Control

The data collected as part of the Non-tidal Network are used in making management decisions regarding Chesapeake Bay water quality as described in the Introduction. DNR follows specific procedures to ensure that the design is properly implemented and that monitoring measurements are made and managed with sufficient accuracy, precision, and detection limits. General discussions of quality assurance and quality control aspects associated with accuracy, precision, data management, reporting, and audits are provided in the subsections below.

Accuracy : The accuracy (closeness to the true value) of the collected data is controlled and assured by the proper use, calibration, and maintenance of both field and laboratory equipment for the measurement of physical and chemical parameters. All instruments are identified by a unique number, used as an index for documentation of

calibration, repair, and preventive maintenance. Daily quality control checks (including the running of blanks and standards) are used to control and assure laboratory accuracy. Accuracy of laboratory results is also assessed through DNR's participation in the Chesapeake Bay Coordinated Split Sample Program (CSSP), a split sampling program in which five laboratories involved in Chesapeake Bay monitoring analyze the coordinated split samples.

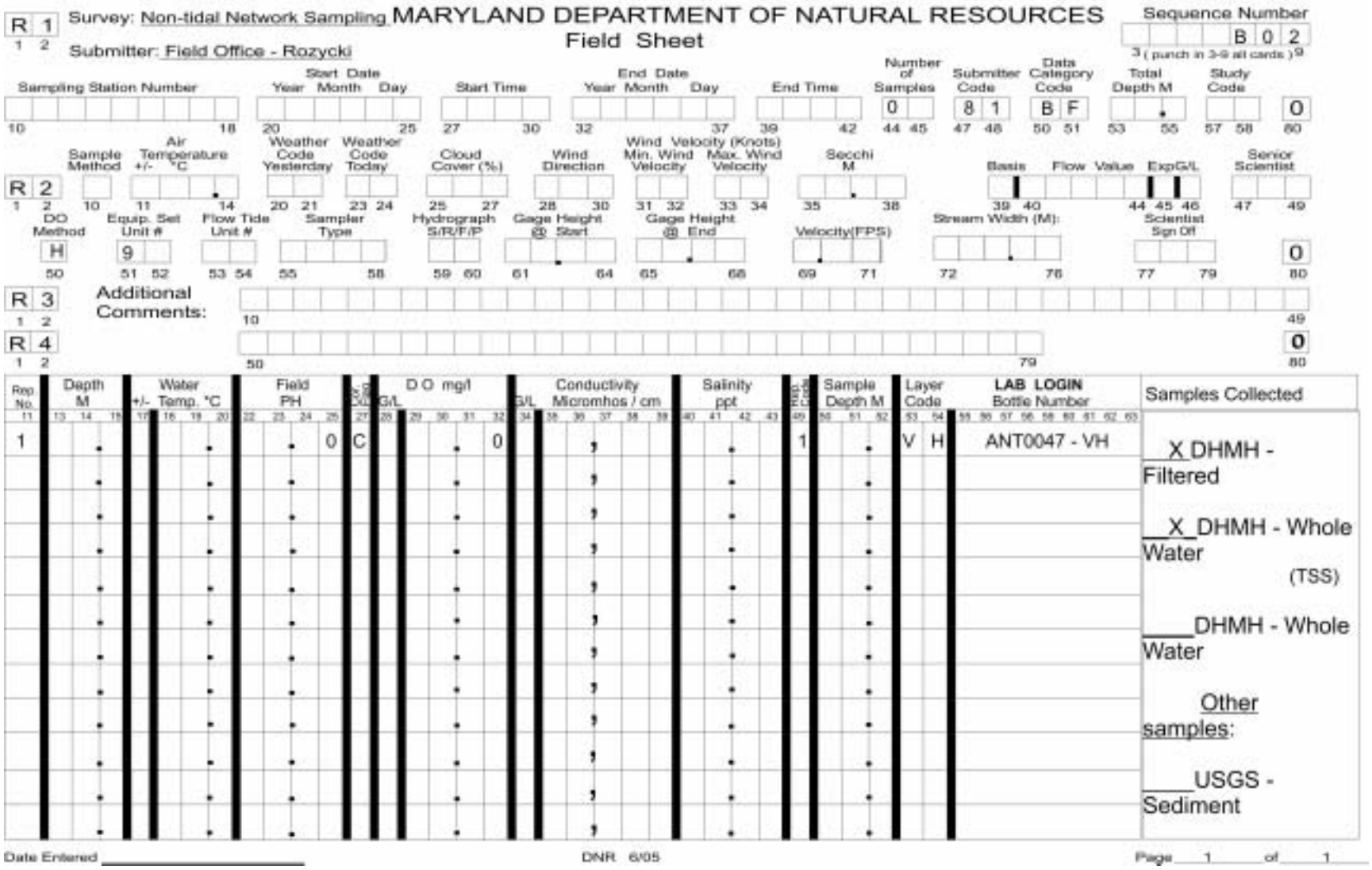
Precision: Precision of the chemical analytical methods is determined and documented from duplicate analyses. Precision of the entire measurement system for laboratory-analyzed parameters, including field processing, storage, and chemical analysis, can be assessed from duplicate field samples. Duplicate field samples are routinely collected approximately every 10 to 20 samples.

Audits: Performance audits for chemical analyses are based on the results of samples distributed by the EPA Chesapeake Bay Program Blind Audit Program. These samples must fall within the 95% confidence interval for acceptance. If results fall outside this range, corrective actions for each parameter and measurement are taken. The DNR Quality Assurance Officer communicates on a weekly basis with the field program staff and confers with the laboratory quality assurance officers to ensure that all aspects of the program are being conducted properly.

Data Management: After field personnel have completed data sheets for a given calendar month, they make a photocopy of the sheets to keep in the Field Office, and send the original field sheets to data management staff at the DNR Tawes Building. The Field Office also generates a Cross Reference Sheet for each set of field sheets, which is sent to the DNR data management personnel along with the field data sheets. The Cross Reference Sheet provides the data management personnel with the documentation to determine what field, nutrient lab and suspended sediment results to expect.

Nutrient laboratory data sheets are also initiated in the field. These nutrient lab sheets list each parameter requested for analysis and include basic information about the sample, such as station, date, time, depth, and volume filtered. The sheets serve as sample transfer sheets, traveling with the samples to the Maryland Department of Health and Mental Hygiene laboratory (DHMH) for nutrient analysis or to the USGS Kentucky Water Science Center for sediment analysis. Both the sheets and the samples are logged in at the laboratory. The analyst reviews the data and, if the data exceed their control limits, the entire run is re-analyzed. Re-analysis can occur for any number of reasons, such as, a poor r-squared on the standard curve, the wrong set of pump tubes (which would provide abnormally low peaks), or high blank values (in the case of DOC). Once laboratory staff has completed the nutrient lab sheets, they are sent to the DNR data management at the Tawes Building.

Figure 3. Non-tidal Network Field Sheet



R 5 study code: 0 9 Replicate:

Maryland Department of Natural Resources

Sequence Number

Survey: NTN: Antietam Creek

Collector: _____

AFO-410-990-4526/C. Rozycki

Laboratory Analysis Sheet (Non-tidal Network Program)

Data Code 1B

Sample Station Number: A N T 0 0 4 7

Date: Year Month Day

Start Depth M: 0.0

End Depth M:

Start Time:

Submitter Code: 8 0

Bottle Numbers:

Type of Sample: Whole (1 quart bottle): A N T 0 0 4 7 V H

Filtered (8 ounce bottle): A N T 0 0 4 7 V H

PC/PN/PP Foils: S E P S H E E T 0

R 6 Sample Method: 6 Data Category Code: B F Sample Layer: V H Field Scientist Sign Off: Date received by Lab Year Month Day: Time Received by Lab: Batch Number: 0

R 7

Check test Required	Parameter Description / Units	Parameter Code	Method Code	Analysis Problem Code	G/L	Results Record Decimal in a Box	Percent Recovery	Standard Deviation	Number in Sample	Analyst Sign Off	
X	TDN as N (F) mg/l	T D N									0
X	Ammonia as N (F) mg/l	N H 4									
X	$NO_2 + NO_3$ as N (F) mg/l	N O 2 3									
X	Nitrite as N (F) mg/l	N O 2									
X	PO_4 as P (F) mg/l	P O 4									
X	Total Dissolved P (F) mg/l	T D P									
X	Dissolved Organic C (F) mg/l	D O C									
	BOD 5 day mg/l	B O D 5									
	Turbidity NTU (W)	T U R B									
	Total Alkalinity (W) mg/l	T A L K									
X	Total Susp. Solids (W) mg/l	T S S									
X	Part. Phosphorus as P mg/l	P P									
X	Part. Carbon as C mg/l	P C									
X	Part. Nitrogen as N mg/l	P N									

Date Reported: Year Month Day

Final Lab sign off

QA/QC sign off

Transcriber sign off

Send Results To:

Bruce Michael
DNR D-2 Tawes Building
Annapolis, MD 21401
bmichael@dnr.state.md.us
410-260-8627

R 8 0

Date Entered: _____

DNR 5/2005

Figure 4. Non-tidal Network Laboratory Analysis Sheet

DNR data management personnel conduct data review and verification at four levels:

At the first level, DNR data management personnel review cross reference sheets and field data sheets: (1) comparing field sheets to cross reference sheets to ensure that all field sheets have been received; (2) reviewing all field sheets to check that they are filled out completely and legibly, and; (3) sending the sheets to a data entry service for keypunch. At the data entry service, the field sheet data are double-entered to minimize errors at the keypunch stage. The entered field data are sent back to DNR as an electronic file on a diskette for further processing.

At the second level, a programmer trainee generates reports and plots for data verification using the Water Quality Import v3 software.

At the third level, system printouts of each data set are sent to a biologist and the Quality Assurance Officer for verification and editing. The Quality Assurance Officer and DNR biologists ensure that measured or calculated information for all types of data are correct and that the codes associated with parameters are properly established.
At the fourth level, data management staff ensure that the overall data verification processes are checked and all data errors are corrected, and that the finalized data sets are created and are formatted to be consistent with historical data sets. The final data set combining the field and lab data is created as an Access database file after completion of data verification processes. This final data set is stored in the designated DNR data base directory on the \TEA\DEVELOPER server for data user access. A formatted submission data set and associated data documentation are also transferred to the Chesapeake Bay Program Data Center on a monthly basis. The data management process is diagramed in Figure 5.

Reporting: Quality assurance information for field duplicate samples in the mainstem and tributaries is stored on the routine computerized water quality data sets as replicate observations that can be used to assess precision. Laboratory quality assurance/control information on duplicates and spikes is stored on a computerized data set at the laboratory.

B6 Instrument/Equipment Testing

A. Teams carry two calibrated Hydrolab meters in case of failure. The meter in use is compared to the reserve meter any time (a) the field scientist recording measurements observes values outside the "typically expected range"; (b) the meter generates variable or erratic values; or, (c) the meter in use displays an error message. If the meters do not agree within acceptable limits, the reserve meter is used. This is noted under special remarks.

B. The specific meter to be used each day of a mainstem cruise received a dissolved oxygen validation check. The meter is set up for a dissolved oxygen calibration, but the oxygen value is only adjusted if drift is greater than 0.4 mg/L.

B7 Instrument/Equipment Calibration and Frequency

The procedures outlined here refer to the Hydrolab instruments. The detailed calibration procedures will be performed as described in the Hydrolab 4000, Surveyor II and Scout II Operation Instructions Manual.

I. Calibration

A. Set up a calibration logbook for each unit, with make, model, and serial number and purchase date. Assign a letter for DNR use as required.

B. Calibrate meters on Friday for use the next week. After one to four days of field use, post-calibrate equipment to determine if any parameter has drifted.

C. Specific conductance calibration shall be made using standards generated by the field office from dry KCl and deionized water. Standards used are 294, 720, 2767, 6668, 12950, and 24820 microsiemens/cm (microsiemens=microS=μS); or 0.002, 0.005, 0.02, 0.05, 0.1, and 0.2 molar KCl, respectively. (At 25 °C microsiemens/cm = micromhos/cm.)

D. A pH calibration shall be made using premixed standards of color-coded pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are specifically labeled (contain expiration dates) and color coded - red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00.

E. Dissolved Oxygen calibration shall be done on the common standard of water-saturated air. After correcting for the barometric pressure and temperature the oxygen content of water-saturated air can be checked against standard DO tables. The DO membrane is also visually checked every time the meter is pre- or post-calibrated. If the membrane appears damaged, the meter is posted as is. Then the membrane and electrolyte are replaced and the meter is calibrated after 24 hours.

F. Record all pre-calibration, post-calibration, and maintenance procedures in the log book, including any values (e.g. barometric pressure) that are used in the calibration procedures. An example of the equipment calibration log is included.

G. Record any unusual circumstances that may affect the Hydrolab unit readings in the logbook.

B8 Inspection/Acceptance of Supplies

N/A

B9 Non-direct Measurements

N/A

B10 Data Management

Reported in B5 above.

ASSESSMENT AND OVERSIGHT

C1 Assessments and Response Action

Field: If a station or specific sample cannot be collected, it is noted on the cross-reference sheet. Specific problems associated with field collection of a site are also noted on the field sheet. Conditions that may affect data results are included in the comments section of the field sheet so that they are available to each data analyst. If post calibration results are outside acceptable limits, the individual calibrating notifies the Field QA Officer who decides if data should be deleted of flagged. If split sample results suggest that there is a problem with the Maryland data, the issue is thoroughly discussed by laboratory and field representatives at AMQAW and possible solutions are offered. The Field QA Officer regularly reviews Equipment Log Books to ensure that all staff are following QC procedures. Standard maintenance recommended by Hydrolab is performed at six-week intervals. All serious Quality Control issues are reported directly to the Field Office Project Chief.

Laboratory: Corrective actions are initiated by the analyst, with the input of the Lead Scientist of the Laboratory Section, if necessary. The Lead Scientist and the Supervisor review corrective actions. A copy of the completed form is submitted to the division QA officer, and the original is kept in the laboratory.

Data Management: The Data Input Editor is the first line of defense for data correction. The DNR Data Clerk reviews all incoming data and compares the data to the cross-reference file. The Data Clerk verifies the submitted data and applies corrections to the physical data-sheet if errors are identified. During the data-import process, the Data Processing Programmer makes all corrections to the data and key fields as they are imported into the WQ Database System. The Data Programmer Analyst assists where needed in constructing better tools to edit and apply to large quantities of data corrections if necessary. Documenting the correction is handled within WQ Maintenance

process. If the correction is fairly generic, edits to the changes are logged. There is no formal documentation for editing data-sheets. These tasks are considered extreme and performed only when confirmed by field office or laboratory personnel.

C2 Reports to Management

Contained in the outline of deliverables in the project Scope of Work. Any changes to the QAPP or to the SOPs referenced herein will be documented and approval of the DNR QA Officer and the WPA Project Officer will be obtained prior to implementation.

DATA REVIEW AND USABILITY

D1 Data Review, Verification and Validation

Field: Described in C1 above.

Laboratory: The DHMH Environmental Chemistry Division uses data review checklists for data validation. Figure 6.

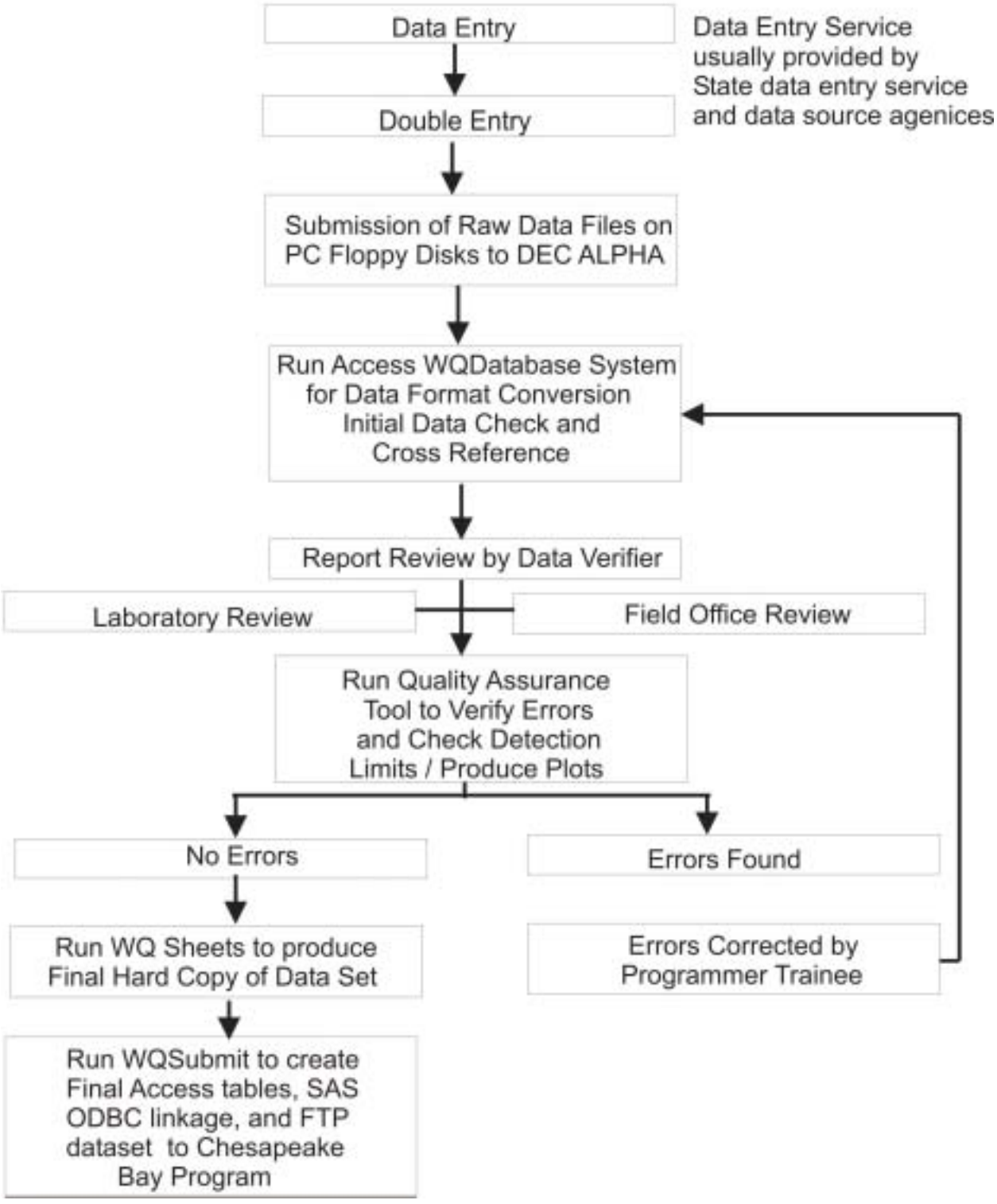
Data Management: The data-management group validates key fields. The key fields insure that the data are accurate and will not be lost or duplicated within the system. After the key fields are validated, the values are plotted to discover any anomalies. The scientists/project managers review the reports and determine if any additional edits are needed to data values. These edits are reported to the data processing programmer who makes the changes. (Figure 5)

D2 Verification Validation Methods

Reported in B5 above.

D3 Reconciliation with User Requirements

Figure 5. Data management flow chart for data entry through production of final master data set



State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY
Nutrients Section

Figure 6. Data Review Checklist

LL Orthophosphate/EPA Method 365.**1**
LL Ammonia/ EPA Method 350.1

Lab Numbers[1]:_____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status *	Comments
Holding Time	48 hours @ 4°C; 28 days @ –20°C		
Samples Analyzed	Within 5 working days		
Calibration Curve	Corr. Coeff. $\geq$ 0.9950		
Reagent Blank	< Reporting Level (0.004 ppm for OP; 0.008 ppm for NH_3)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples		
	Recovery = 90–110%		
External QC[2]	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Concentration = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RSD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.004–0.250 ppm for OP; 0.008–0.500 ppm for NH_3)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

REFERENCES

U.S. Environmental Protection Agency (EPA). 1996. ***Recommended Guidelines for Sampling and Analysis in the Chesapeake Bay Monitoring Program***. Chesapeake Bay Program, August 1996. CBP/TRS 148/96; EPA 903-R-96-006.

U.S. Environmental Protection Agency (EPA). 1991. ***Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines*****,** ***May 1991***. Chesapeake Bay Program: Annapolis, MD. CBP/TRS 58/91.

Quality Assurance Project Plan for the Maryland Department of Natural Resources Chesapeake Bay Water Quality Monitoring Program Chemical and Physical Properties Component for the period July 1, 2005 - June 30, 2006. Bruce Michael and Beth Ebersole

Non-tidal Network Program Standard Operating Procedures. July 2005. Maryland Department of Natural Resources. 17 pp.

APPENDIX I

Maryland Department of Natural Resources

Non-tidal Network Program
Standard Operating Procedures

Prepared by: _____ Date: _____
Natural Resource Biologist

Reviewed by: _____ Date: _____
Natural Resource Biologist

Approved by: _____ Date: _____
Water Quality Monitoring Program Chief

July 2005

Table of Contents

MD-DNR
Non-tidal Network Program Protocols

Maryland's Non-tidal Water Quality Monitoring Network currently includes 10 load sites where nutrient and sediment concentrations are sampled monthly during base flows, as well as 8 times throughout the year during high flow events. An additional 4 stations have been added to the network as secondary sites. The secondary sites will only require monthly sampling, and will not be sampled during high flow events.

Load Sites: GEO0009, ANT0047, MON0546, BEL0053, TUK0181, WIL0013, NPA0165, GWN0115, DER0015 and TF1.2

Secondary Sites: CAC0148, PXT0972, GUN0258, and RCM0111

Procedure: We will use a modified version of the USGS equal width interval assignment for our load sites. The PA USGS modified protocol reduces the number of verticals collected from 10 to a lower number based on the width of the stream being sampled.

Width of Waterway (ft.)	Minimum # of Verticals
0-25	1
25-100	3
100-250	5
250-500	7
>500	9

The number of verticals that will be used for MD-DNR sampling is dependant on the width of the stream at the time of sampling. The PA USGS modification assumes that the number of verticals required can be reduced because the stream is well mixed across the horizontal direction. To check this assumption each time a station is sampled four in-situ parameters (oxygen, pH, specific conductance and temperature) will be determined at each selected vertical sampling point. If the stream appears well mixed, the composite sample will be collected from vertical samples drawn at these selected sampling points. In addition, the variability across the stream will be checked every one to three years. Running the full nutrient suite on a sample generated at each vertical sampling point and on the normally generated vertical/horizontal composite will do this. If variability is excessive, additional vertical sampling points (max 10) will be required for that station.

Once stream variability has been assessed, collection of a water sample that is both horizontally and vertically integrated will begin. If the maximum stream

velocity observed is greater than or equal to 1.5 ft/sec and under 7.0 ft/sec an isokinetic equal width increment (EWI) composite sample will be generated using an approved USGS sampler (DH-59, DH95, or DH81). If maximum stream velocity is under 1.5 ft/sec a non-isokinetic equal width increment composite sample will be generated using an approved USGS sampler (WBH-96 or modified DH81). At this time, no sampling method for velocities over 7 ft/sec has been developed.

The EWI composite sample will be generated by collecting individual depth integrated samples at each specified vertical sampling point. These samples will be composited in either a 4L or 8L churn splitter. Two to three sample bottles will then be drawn from the churn splitter for field processing and /or delivery to the appropriate laboratory. One sample bottle will be processed in the field to generate both filter pads for the particulate nutrient parameters and a bottle of filtered sample water for the dissolved nutrient parameters. A second bottle will be filled for TSS analysis. All of the water in the TSS bottle will be used for the analysis. The Maryland Department of Health and Mental Hygiene (DHMH) will analyze the TSS samples. During storm events a third sample will be drawn and sent to the USGS Sediment Lab in Kentucky for suspended sediment analysis.

Please see the Hydrolab Sampling Procedures for a detailed explanation of how the in-situ parameters are sampled.

Please see Non-tidal Network Program Sampling Procedures for details on the collection of the EWI composite sample.

Please see the Non-tidal Network Program Sample Processing for a detailed explanation of how the field samples are processed.

Samples collected: Depth integrated samples collected at the vertical sampling points will be composited in the churn splitter. Sub-samples will then be dispensed from the churn splitter and used to generate:

One 500 ml HDPE bottle of whole water for Suspended Sediment analysis at the USGS Sediment Lab in Kentucky (only during storm events).

One TSS whole water bottle 30ml to 225 ml (volume dependent on turbidity)

One HDPE 2 quart nutrient sample bottle that will be field processed into:
- Two 25mm GF/F 0.7 micron Particulate Carbon/Particulate Nitrogen filters
- Two 47mm GF/F 0.7 micron Particulate Phosphorus filters
- One 8 or 16 ounce HDPE bottle of filtrate for dissolved nutrient analysis

SAMPLE QA/QC

One Source Solution Blank must be submitted for each sampling day.
One Duplicate Stream Sample is processed every 10 to 20 samples.
One Deionized (DI) Water Equipment Blank is processed once a month.

Source Solution Blank

Each day a 16 ounce filtrate HDPE bottle must be filled from one of your vehicle Deionized Water bottles. This will be sent to DHMH with your sample filtrate bottles for dissolved parameter analysis. Label the 16 ounce bottle with "DI Filtrate Blank", the date and your initials. Rinse this three times with DI water and then fill ¾ full with DI. Add date, time filled and your initials to DI Blank Lab sheet in the field pack. Send Results To: should list "Sally Bowen" and be highlighted. Ice and ship with regular filtrate samples. Results will be reviewed by the Field Office Chief. Repeat problem parameters will be discussed with Principal Investigator and corrective solutions will be explored.

Duplicate Sample

A replicate sample will be processed from the churn splitter every 10 to 20 samples. It will be drawn from the same churn splitter as the original sample and processed identically. See Churn Splitter Sub-Sampling Procedure and Non-tidal Network Program Sample Processing for a detailed explanation of these processes. Results will be reviewed as part of MD DNR duplicate data set.

DI Blanks: Processed and Unprocessed

One sampling team per month must process and submit an equipment blank. The churn splitter will be thoroughly rinsed with DI water. Then it will be filled with DI water. One DI Nutrient Only 2 quart sample bottle will then be drawn from the churn splitter and processed for particulate and dissolved nutrients. Process this bottle in the same way that stream samples are processed. Generate filtrate, PC/PN filters and PP filters. No DI Blank is submitted for either Suspended Sediment or TSS. Label the Processed Blank as Pxxx Filtrate (with xxx = filter unit) and add the date. Also submit an Unprocessed Blank as UPxxx Filtrate by labeling, rinsing 3 times, and then filling a filtrate bottle with DI water. Fill from the same DI bottle you used for the Processed Blank. Place 2 blank filters each for PC/PN and PP in the Unprocessed Blank foil squares. See Churn Splitter Sub-Sampling Procedure and Non-tidal Network Program Sample Processing for a detailed explanation of these processes. Add date, time processed, your initials and either Pxxx or UPxxx in the sample bottle line on the DHMH lab sheets in the field pack. A separate sheet must be submitted for processed and unprocessed samples. Send Results To: should list "Sally Bowen" and be highlighted.
Ice samples and ship with regular stream samples. Results will be reviewed by the Field Office Chief. Problems will be discussed with the Project Officer and potential solutions explored.

Non-tidal Network Program Sampling Procedure

1. You will need to record the time and gage height at the beginning and end of the sample collection period on the field sheet. If you are sampling at the exact location of the gage, open the gage house and record the gage height and time before sampling and after you finish collecting samples. If you will not be sampling at the exact gage location stop at the gage and record a beginning gage height and time. If the gage is on-line you can get the end reading from the USGS web page. Check the recorded gage height against the cross reference list in the field pack to determine if maximum velocity expected is greater than or equal to 1.5 ft/sec. **If YES,** an isokinetic composite sample **MUST** be collected. If the maximum velocity is under 1.5 ft/sec or over 7.0 ft/sec a non-isokinetic composite sample is collected.

2. Set up cones on the road to block off enough room so that you feel safe on the downstream side of the bridge. Wear your orange safety vest.

3. Measure stream width by placing the measuring tape along the bridge from stream bank to stream bank. Measure from left to right looking downstream. Establish the number of increments (transects) you will sampling by using the table on page 3. After you determine the number of increments (transects) that will be sampled, use the formula below to determine the location of each vertical sample. A more detailed explanation of the new isokinetic sampling protocols can be found in the Non–tidal Field Pack. Check "Sampling Procedures and Protocols for the Chesapeake Bay Non-tidal Water Quality Network" report, page 6 or the USGS procedures.

   Here is a formula to determine the number of transects and the location of verticals:

   - Stream Width / number of transects = transect length
   - 1^{st} vertical = Transect length / 2
   - 2^{nd} vertical = Transect length + 1^{st} vertical
   - 3^{rd} vertical = Transect length + 2^{nd} vertical
   - 4^{th} vertical = Transect length + 3^{rd} vertical
   - 5^{th} vertical = Transect length + 4^{th} vertical

   For example, if the stream is 60 feet wide and it is divided into 3 transects, the 1^{st} sample should be taken at 10 feet from the left bank (while facing downstream), the 2^{nd} at 30 feet, the 3^{rd} at 50 feet. Record vertical locations in the comment section of the field sheet.

4. Once you have established a location for each vertical, record Hydrolab readings for each vertical by immersing the Hydrolab in the stream directly (if equipment and stream velocity are suitable) or by collecting a

rinsed bucket at each vertical. Refer to Hydrolab Sampling Procedures for a detailed explanation of this process. Review these readings. The stream is well mixed if no set of readings for any one parameter differs by 20 %. If the stream is well mixed, record the median value for each parameter on the field sheet and begin collecting samples.
If stream is not well mixed, increase the numbers of verticals by at least two and repeat steps 3 & 4.

5. Based on the stream velocity and sampler choices available, choose a sampler to use. Rinse the sampler collection bottle and all whole water sample bottles three times with stream water (directly in stream or from a freshly collected bucket of stream water). Rinse the churn splitter with 2 to 4 L of stream water. Run a liter of water through the spigot.

1) DH-59 (Brass, hand-held isokinetic sampler with a fixed nozzle.)

A. Follow instructions 1 – 5 under Non-tidal Network Program Sampling Procedure.

B. Put glass collection bottle into sampler by pulling on the hook at the bottom, place the mouth of the bottle in first and then slide the bottom in. Make sure there is a good seal around the mouth of the bottle.

C. Decide who will be the clean hands person (who handles the sample) and who will be the dirty hands person (who handles the equipment). The clean hands person must wear rubber gloves during the sampling. They will only touch the sample bottle and churn splitter.

D. If the stream looks deeper and faster in one area, establish your transit rate at that spot before starting to sample. Remember, if the sampler collection bottle is over-filled (more than ¾ full) at any of the verticals using the transit rate you establish initially, you must discard all sample water in the churn splitter and begin sampling over again. The sampler collection bottle must still be bubbling when it reaches the surface. The DH-59 fills very slowly. Try to go at the slowest, steady rate you can while filling the bottle. It most likely will take more than one dip to fill the collection bottle. If the collection bottle is less than 40% filled after the first up/down pass, you can lower and raise it again before you empty it into the churn splitter. Remember total amount collected must be ¾ or less. **If you decide to do multiple dips, you must do the same number of dips at each vertical sampled.**

E. Once you establish your transit rate and number of dips, you are ready to collect the first vertical. Lower the sampler until the back fin is touching water surface. Wait until it orients towards the flow and lower the sampler at the established transit rate. When you feel it touch the bottom,

automatically begin to raise the sampler to the surface at the same transit rate it was lowered. Repeat, if doing multiple dips.

F. Raise the collected sample. The dirty hands person should set the sampler on the ground in a steady position and the clean hands person should then retrieve the bottle from the sampler and empty it into the churn splitter.

G. Move the sampler to the next vertical location. Repeat steps E & F for each vertical.

H. Continue this process until the verticals for all transects have been completed. The churn splitter must contain enough water to process all the samples. If necessary you can return to each vertical location and collect an additional sample if more water is needed. Remember, the churn splitter cannot be overfilled!!! If it does overfill, you must empty the churn splitter and begin the sampling over again.

I. Follow the instructions under Churn Splitter Sub-Sampling Procedure at the end of this section.

2) WBH-96 (Weighted bottle, hand held, non-isokinetic sampler)

A. Follow instructions 1 – 5 under Non-tidal Network Program Sampling Procedure.

B. Put the plastic liter size collection bottle in the sampler and place the elastic around the neck of the bottle making sure it is secure.

C. Decide who will be the clean hands person (who handles the sample) and who is the dirty hands person (who handles the equipment). The clean hands person must wear rubber gloves during the sampling. They will only touch the sample bottle and churn splitter.

D. If the stream looks deeper and faster in one area, begin there. Remember, if the sampler collection bottle is over-filled (past the neck of the bottle) you must discard the sample water and begin again. The sampler collection bottle must still be bubbling when it reaches the surface.

E. Lower the sampler until the bottom of the sampler is touching the water surface. Begin lowering the sampler and when you feel it touch the bottom, automatically begin to raise the sampler to the surface.

F. Raise the collected sample. The dirty hands person should set the sampler on the ground and the clean hands person should then retrieve the bottle from the sampler and empty it into the churn splitter.

J. Continue this process until the verticals for all transects have been completed. The churn splitter must contain enough water to process all the samples. If necessary you can return to each vertical location and collect an additional sample if more water is needed. Remember, the churn splitter cannot be overfilled!!! If it does overfill, you must empty the churn splitter and begin the sampling over again.

G. Follow the instructions under Churn Splitter Sub-Sampling Procedure at the end of this section.

3) DH-81 (Hand held wading sampler, optional isokinetic/ non-isokinetic)

If stream velocity is ≥1.5 ft/s and considered safely wadable, you may use the DH-81 as an isokinetic sampler by using the appropriate nozzle (usually 5/16"). If flows are less than 1.5 ft/s the DH-81 may be used without the nozzle to obtain a grab sample.

A. Select the area of stream that you will be sampling and secure the tape measure across the stream. Measure from left to right looking downstream. Establish the number of increments (transects) you will be sampling and location across the transect where you will be collecting your vertical sample based on the width of the stream.

B. Once you have established a location for each vertical, record Hydrolab readings for each vertical. Have one person on the stream bank recording the numbers while the other person handles the Hydrolab. See Hydrolab Sampling Procedures for a detailed explanation of the process.

C. Rinse the DH-81, including bottle, nozzle (if needed), cap and the churn splitter in the stream. Make sure you are downstream of the sample area to ensure that you do not stir up the streambed prior to sampling.

D. Assemble the DH-81 by screwing the cap onto the liter sample bottle and attach the nozzle to the cap (if the steam velocity is under 1.5 ft/sec you can sample without the nozzle). Secure the DH-81 to the wading rod by snapping it into place over the cap.

E. Decide who will be the clean hands person (who handles the sample) and who is the dirty hands person (who handles the equipment). The clean hands person must wear rubber gloves during the sampling. They will only touch the sample bottle and churn splitter.

F. Enter the stream down river of the sampling location and walk up to the sampling location in the centroid (maximum) of the steam flow. Raise and

lower the sampler at a constant rate such that the sample bottle is ½ - ¾ full when breaking the surface.

G. **If the sample bottle is too full pour out sample and speed up your transit rate or use a smaller nozzle or a combination of both until the sample bottle fills ½ - ¾ when the sampler is raised out of the water column. Likewise, if the sample is not full enough, pour out the sample and use a larger nozzle or slow your transit rate to increase sample volume.**

H. Empty the collected sample into the churn splitter. Move to the next vertical and repeat the collection process.

I. Repeat the sample collection process until there is sufficient volume to fill the 4 or 8 Liter churn splitter.

J. Follow the instructions under Churn Splitter Sub-Sampling Procedure at the end of this section.

4) Bucket Sampling

Note: If D.O. and Temp are read from a bucket sample YOU MUST Enter a B in the G/L box associated with D.O. so that these values are deleted from data sent to CBP.

Bucket samples are taken from bridges. A sample may be collected to provide stream rinse water for sampling equipment and whole water bottles. If in-situ readings cannot be made by immersing Hydrolab directly in the stream you can collect a bucket from each vertical point for readings. See note above.

A. Select the appropriate length of rope for the bridge from which you will be sampling and secure tightly to bucket.

B. Chose a vertical sampling location to sample.

C. Lower the bucket to the water.

E. Tip the bucket and fill with enough water to rinse the bucket (at least a few inches).

F. Depending if it is a high or low bridge, you may want to shake the rope to expel the rinse water from the bucket, or pull the bucket back up to dump the rinse water out of the bucket. Rinse three times.

G. Fill the bucket.

H. Pull the bucket back up, making sure the rope does not rub against the side of the bridge. This can sometimes cause dirt, rust, paint, etc to fall into the sample.

I. Immediately carry the bucket back to the van. Rinse equipment or go to J.

J. If using for in-situ readings immerse the Hydrolab sonde in the bucket, swirl at 1 ft/sec. Record readings. Repeat for all verticals. Remember to record a “B“ in G/L box for D.O.

Churn Splitter Sub-Sampling Procedure

The following steps are to be completed for filling of all sample bottles from the churn splitter:

A. Set the churn splitter in an area where the spigot is easily accessed to dispense water.

B. One person should churn the sample, while the other person fills the sample bottles from the churn splitter.

C. Churn the sample at 9 inches per second.

D. Do not break the water surface with the wand while churning.

E. Churn the sample a minimum of 10 times before dispensing water.

F. Continue to churn the sample until all the sample bottles are filled. Samples cannot be dispensed if the water level is at or below the spigot.

G. Dispense whole water sediment related samples first. Dispense:
   a. SSC (storms only)
   b. TSS
   c. Nutrient Filtration Bottle

   Note: After filtering for PC/PN if the sample volume originally chosen for the TSS sample is too small or too large, discard and dispense a TSS bottle with a better volume.

G. Process sample bottles filled as per the instructions under Non-tidal Network Program Sample Processing.

CHURN SPLITTER CLEANING PROCEDURE

After all samples are collected and processed empty churn splitter and rinse well with DI water. Rinse sampler collection bottle with DI. If any of the sample collection equipment needs to be reused before it can be cleaned at the office, follow procedure below.

A. Soak equipment in 10% Liquinox Solution for 20 – 30 mins. If churn splitter is being cleaned fill it with Liquinox and add collector bottle and nozzles. Let sit while completing station or while driving to next station. There is a small cup for soaking just nozzles in the field tub.

B. After soaking, scrub with brush provide and rinse completely with tap water. Rinse three times with DI. Air dry and store in clean baggies or use again.

Non-tidal Network Program Sample Processing

A. Laboratory Supplies

Pads

a) PC/PN
The pads used for PC/PN samples come directly from DHMH. The PC/PN pads are pre-combusted (490 ^{o}C), 25mm Whatman GF/F glass fiber filters – pore size 0.7 µm. Two PC/PN pads are used per sample.

b) PP
The pads used for PP samples are 47mmWhatman GF/F glass fiber filters - pore size 0.7 µm. Two PP pads are used per sample.

B. Particulate sample filtration, processing and storage

1. **Particulate Carbon/ Particulate Nitrogen (PC/PN)**
   a) To generate PC/PN filters first clean two 25mm bells with deionized (DI) water. Set up unit for filtering. Be sure that there is a trap in line between the manifold and the vacuum source.
   b) Place a pre-combusted 25 mm GF/F filter (pore size = 0.7 µm) on each filter frit. Always use clean forceps when handling the filter pads.
   c) Using the two quart whole water sample drawn from the churn splitter **(please see Section D- Churn Splitter Sub-Sampling Procedure)** mix sample thoroughly by agitating and shaking the sample bottle vigorously, then rinse graduated cylinder three times with sample.
   d) Agitate the sample again before measuring in the graduated cylinder. Fill graduated cylinder with sample and filter desired volume through filtration unit. Be sure to use a graduate that is close to the volume being filtered (ex: if you are only filtering 80 ml of sample use a 100 ml graduate). Keep the vacuum pressure below 10 inches of Hg (around 8" Hg is good).
   e) Filter 10-200 ml through each filter. Filter enough sample to leave noticeable color on the filter pad.
   f) Make sure filter is sucked dry and the **same volume is filtered for both pads**.
   g) Record the volume filtered (total volume through one pad - do not add the volumes for the 2 pads together) on the foil square.

   NOTE: Samples for dissolved parameters are not to be collected from this filtrate.

   h) Using forceps, fold each filter in half.
   i) Place both filters in a foil square labeled with date, station, sample layer, PC/PN, and volume filtered. Be sure that the pads are not overlapping in the foil square to keep them from freezing together.
   j) Place pad in pre-marked foil square, and carefully fold foil square in thirds, horizontally. Then fold the ends in to seal the filter inside. Be

sure forceps do not touch sample residue on the filter pads, because the sample will adhere to the forceps. Place the folded foil in a zip-lock bag or pad container, and put it in a cooler on ice.

k) Upon return to the Field Office, place the foils in their appropriate zip-lock bag in the sample freezer and place the bag in the DHMH bin. Put the completed volume sheet in the bag with the foils.

2. **Particulate Phosphorus/ Particulate Inorganic Phosphorus (PP/PIP)**

a) To generate PP filters, clean two 47mm bells with deionized (DI) water. Set up unit for filtering. Be sure that there is a trap in line between the manifold and the vacuum source. The filters used are two Whatman 47 mm GF/F filters.
b) Using the two quart whole water drawn from the churn splitter filter 50 ml of sample through each filter pad.
c) Use the filtrate as an equipment rinse and discard.
d) Then filter enough additional (another 50 - 750 ml) to leave a noticeable color on the filter pad.
e) Record the **total** volume filtered through each pad being sure to add the 50 ml rinse water (total volume through one pad – do not add the volumes for the 2 pads together) on the foil square.
f) Use this filtrate to fill up the container for the dissolved parameter analysis. See section C (Filtered dissolved nutrient sample collection) below.
g) After collecting filtrate, make sure filter is sucked dry.
h) Rinse the filter pad using at least three - 10 ml rinses of DI water sucking the pad dry after each rinse.
i) Using forceps, fold each filter in half.
j) Place both filters in a foil square labeled with date, PP, station, sample layer, and volume filtered (this is the total volume of sample through each pad, including the initial 50 ml rinse). Be sure that the pads are not overlapping in the foil square to keep them from freezing together.
k) Fold the foil square as described in step B.1.i. above. Place foil square in zip-lock bag or pad container, and put in the cooler on ice until you return to the field office.
l) Upon return to the Field Office, place the foils in their appropriate zip-lock bag in the sample freezer and place bag in the DHMH bin. Put the completed DHMH volume sheet in bag along with the foil squares. Frozen samples are delivered Friday of sampling week so Lab can analyze within 28 days of collection.

C. Dissolved nutrient sample filtration, collection & storage

NOTE: The filtrate collected for this sample must come from the PP filtration set-up. If you cannot get enough water through these pads to fill the filtrate sample bottle, then use more GF/F filters to get enough filtrate. The filtrate may not come from pads that are pre-combusted (PC/PN).

The following steps are to be completed for collection of all filtrate:

a) Run 50 ml of sample water through the filter.
b) Use this 50 ml of filtrate to rinse the flask and then discard.
c) Run more sample water through the filter and collect in the flask.
d) Rinse 8 oz or 16 oz HDPE bottle and cap three times with filtrate.
e) Fill the bottle with filtrate and replace cap. If sample will be frozen before delivery to the lab do not fill more than ¾ full.
f) Store the bottle on ice in a cooler. Deliver to the courier or directly to DHMH at the end of the field day. If you miss the courier filtrate sample bottles may be frozen and delivered on Friday directly to DHMH. If freezing the filtrate sample, copy the regular DHMH Lab Sheet and place the copy in a zip-lock bag with the filtrate bottle. Lab must analyze unfrozen sample within 24 hrs of collection; frozen sample within 28 days.

D. Total Suspended Solids (TSS) collection and storage

a) Chose the appropriate size sample bottle.** Label with Station Id, date and TSS ONLY. Rinse cap and bottle three times with sample water. Bottle may be rinsed from a Rinse Only bucket of water.
b) Fill bottle with sample from the churn splitter. Theoretically the TSS bottle should be filled before the nutrient bottle. Follow the Churn Splitter Sub-Sample Procedures. Because DHMH will be sampling the entire amount we send them, you cannot dump any water out once you fill the container.
c) Ice sample. Deliver directly or send by courier to the DHMH within 48 hrs. An original completed DHMH Lab Sheet must accompany the sample. Note: If you are sampling on a weekend or miss the courier since the holding time for TSS samples is 48 hours the sample can be sent by courier the day after you collected it OR delivered directly to the Lab within 48 hours of collection.

** Note: DHMH will be using all the water in the TSS sample bottle to generate the TSS filter. DO NOT SEND THEM TOO MUCH WATER. The DHMH uses 25 mm filters for TSS. Fill the TSS Sample Bottle with the same amount of water that you expect to use for the PC/PN filters. REMEMBER the Lab will need to rinse their TSS filters THREE TIMES. There are 30ml, 60ml and 225ml bottles in the field tub to use for the TSS sample. The 30 and 60 bottles are graduated. The 225 ml bottle can be filled to any estimated volume.

E. Suspended Sediment Concentration (SSC) collection and storage

a) Label 500ml plastic Nalgene bottle with Station ID, date and time.
b) Fill bottle to shoulder from churn splitter. Follow the Churn Splitter Sub-Sample Procedure instructions. No water can be dumped from the filled Nalgene bottle. **This sample must be the first sample taken from the churn splitter.**

c) Mark water level line on the Nalgene bottle with a Sharpie.
d) Sample does not need to be iced but should be kept in dark. Place in the box labeled “Sediment Samples” when you return to the office. Samples will be shipped quarterly to the USGS Sediment Lab in Kentucky. Note: Each year (Oct-Sept.) all samples must be shipped by September 30th.

Hydrolab Sampling Procedures

Make sure the Hydrolab has been turned on for at least 15 minutes prior to sampling. Submerge the Hydrolab sonde directly in the stream to obtain the required readings. If flow is too swift or your meter is not practical for in-situ readings obtain readings from a bucket grab. Add B in G/L box for DO and note "Bucket Readings" in "Comments" on Field Sheet.

1. Remove plastic storage cup from the Hydrolab, check DO membrane to make sure it is clear and there are no bubbles.

2. Protect probes by installing probe guard or stirrer if flow will be under 1 fps for any in stream measurement point .

A. Sampling in the bucket: (Remember "B" in DO G/L box

a) Follow steps 1 and 2 above.
b) Swirl the Hydrolab in the bucket at 1 fps until the readings stabilize.
c) Record readings on the field sheet.
d) Remove the Hydrolab from the bucket, and rinse probes with deionized water before replacing plastic storage cup.

B. Sampling from the bridge:

a) Follow steps 1 and 2 above.
b) Turn on the circulator from the Hydrolab display menu.
c) Lower the Hydrolab over the bridge at the first vertical. Position the probes at mid-depth for the vertical.
d) Wait for the readings to stabilize and record them on the field sheet.
e) Carefully raise the Hydrolab back up and move to the next vertical.
f) Repeat steps c through e until all the verticals have been sampled.
g) Remove guard. Rinse probes with DI. Replace storage cup.

C. Sampling while wading:

a) Follow steps 1 and 2 above.
b) Turn on the circulator from the Hydrolab display menu.
c) Place the Hydrolab directly in the water at the first vertical. Position the probes at mid-depth for the vertical.
d) Wait for the readings to stabilize and record them on the field sheet.
e) Repeat steps c and d until all the verticals have been sampled.
f) Remove guard. Rinse probes with DI. Replace storage cup.